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- (21) Application No 7918628 (54) Curable solventless organo-polysiloxane compositions
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- (57) A reactive diluent of the formula:
 $[CH_2 = CH(CH_3)_2SiO]_xSi(C_6H_5)_2$
is added to an organopolysiloxane composition in which the organopolysiloxane has at least 8 Si atoms and 67 to 85 mol % $C_6H_5SiO_{3/2}$ and 33 to 15 mol %
 $CH_2 = CH(CH_3)_2SiO_{1/2}$
units, containing both platinum catalyst and a silicon hydride cross-linker, so as to give good handling properties combined with valuable mechanical properties.

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EFFECT OF VARYING AMOUNTS
OF $(\text{OViMeSi})_2\text{O}$ FLUID IN THE
RESIN.

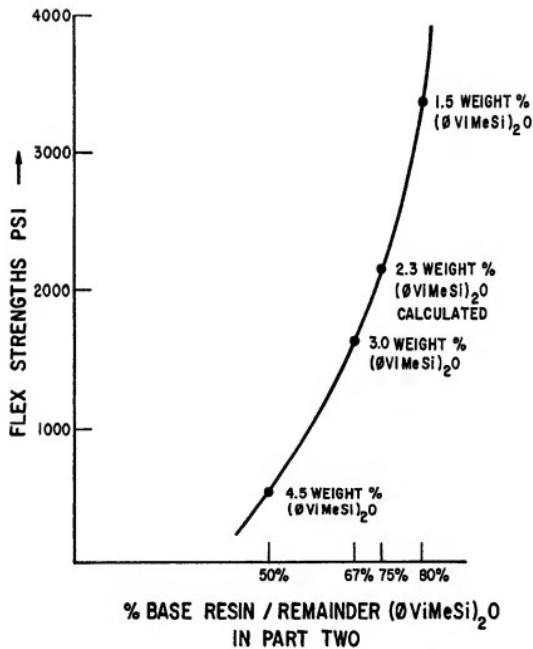


FIG. I

SPECIFICATION

Curable solventless organopolysiloxane compositions

- 5 The present invention relates to curable organopolysiloxane resins containing a reactive diluent. Organopolysiloxane resins in which the substituent organic groups are methyl, phenyl, vinyl and/or similar organic groups are well-known. These materials cure through a variety of mechanisms, such as peroxide catalysed vinyl groups on silicon or by the platinum catalysed addition of silicon hydride to alkenyl groups on silicon. The properties of these organopolysiloxane 10 resins such as toughness and retention of strength at high temperatures make them useful in casting resin applications.

The resins that are useful for casting applications are those that have relatively high viscosities, of the order of 5.0 to 200 Pa·s or higher. These resins, even though they have the desired strengths, have one important disadvantage. Because of their high viscosities, they are 15 extremely difficult to handle in use. They do not pour rapidly and have slow flow when cast into place.

The problem is, therefore, posed as to how one can use the high viscosity resins for their desirable properties and at the same time obtain desirable handling properties.

An obvious solution is to dilute the resins with solvent but this approach leads to bubble 20 entrainment when the casing resin is heated to cure it. It also leads to the time-consuming step of solvent removal from the cast resin.

Most recent attempts to solve the handling problem have been to incorporate a low molecular weight cross-linker in the system. For example, Clark in U.S. Patent 2,894,930 shows a one-part, curable casting resin wherein he suggests using

25 $(CH_2 = CH(CH_3)_2SiO_2Si(C_6H_5)_2$

as a portion of the reactive alkenyl-containing resin. The materials are cured through the use of 30 peroxide catalysts. These materials have the advantage of being one-part, that is, all the essential ingredients can be mixed together and stored without the material curing. The disadvantage, of course, is the fact that the peroxide-cured, one-part materials require a long period of time to cure.

Mink *et al.*, in U.S. Patent 3,944,519, overcomes the latter problem by increasing the rate of 35 cure of such resins by changing the cure system from the peroxide-cured vinyl to the platinum catalysis of the silicon hydride addition to alkenyl groups i.e.:



40 Thus, Mink *et al.* utilized low molecular weight (low viscosity) silicon hydride cross-linker organopolysiloxanes in a vinyl-containing organopolysiloxane to enhance the cure rate and also to reduce the viscosity of the vinylsiloxane resin so that it could be easily handled. The patent teaches that only specific silicon hydride containing crosslinkers work. The use of low molecular weight vinyl-containing diluents is not shown or suggested therein.

45 We have now found that by adding a specific low molecular weight vinyl-containing diluent, lower viscosities of the casting resins can be obtained without sacrificing the desirable mechanical properties of the higher viscosity casting resin.

This invention consists in an improved curable composition consisting essentially of a mixture of (a) an organopolysiloxane containing from 67 to 85 mol percent $C_6H_5SiO_{3/2}$ units and 33 to 50 15 mol percent of $CH_2 = CH(CH_3)_2SiO_{1/2}$ units; said organopolysiloxane having an average of at least 8 silicon atoms per molecule; (b) a silicon hydride containing polysiloxane crosslinker for (a), said component (b) being present in an amount sufficient to provide from 0.9 to 1.1 mol of silicon hydride per mol of $CH_2 = CHSi$ present in (a) and (d); (c) a platinum catalyst in an amount sufficient to catalyse the reaction of the silicon hydride with the $CH_2 = CHSi-$; and (d) a reactive 55 diluent having the formula:



In the composition, the organopolysiloxane resin (a) the base resin. The feature of resin (a) is 60 that it has a sufficiently high viscosity to give the desired mechanical strength to the cured composition. The resin (a) is essentially the same as that described in Mink *et al.*, discussed above, and consists of monophenylsiloxy units in the range of from 67 to 85 mol percent; and dimethylvinylsiloxy units in the corresponding range from 33 to 15 mol percent. It is preferred that the resin (a) should have 75 mol percent of monophenylsiloxy units and 25 mol percent of 65 the dimethylvinylsiloxy units.

The resin is easily prepared by conventional hydrolysis of the corresponding chloro- or alkoxy silanes and conventional condensation techniques. Although there does not appear to be any upper limit on the molecular weight of the resin (a), it should have a degree of polymerization of at least 8 silicon atoms per molecule. This is to ensure adequate physical 5 strengths in the final product. The resin (a) can also be treated, for example, by alkaline condensation catalysts, to reduce the silanol content of the resin.

The silicon hydride containing the siloxane (b) serves as a crosslinker and curing agent in the 10 curable composition. This material can be any silicon hydride containing silane or siloxane that is compatible and gives the cured composition the desired properties. The material may be, for example, the polymer found in the Mink *et al.* U.S. Patent at column 2, lines 23-25 or



The crosslinker must have at least two (2) silicon hydrogens per molecule. There must be 15 enough of component (b) present to give from 0.9 to 1.1 mol of silicon hydride per mol of alkenyl group in the curable composition. Preferred a ratio of 1 mol of silicon hydride to 1 mol of alkenyl is preferred for the best results. The crosslinker (b) can be prepared by conventional techniques known to those skilled in the art, for example, the cohydrolysis of the corresponding silanes.

20 The platinum catalyst (c) can be any of the well-known forms of catalytic platinum, ranging from finely divided platinum metal to platinum on various carriers to the chloroplatinic acid and complexed platinum compounds. Chloroplatinic acid in a small amount of solvent or $[(\text{R}_3\text{P})_2\text{PtCl}]_2$ where R is methyl, ethyl, propyl or butyl is preferred.

There should be at least 0.1 part by weight of platinum per million parts by weight of the 25 combined total of components (a), (b) and (d) and 1-20 parts pt per million parts are preferred.

The unique component of this invention is the component (d), the vinyl containing siloxane diluent:

30 $[\text{CH}_2 = \text{CH}(\text{CH}_3)_2\text{SiO}]_2\text{Si}(\text{C}_6\text{H}_5)_2.$

On mixing the diluent (d) with the component (a) in a ratio of (d) to (a) of from 20/80 to 50/50, a solventless material is produced which has a maximum viscosity of about 2.5 Pa·s. The preferred ratio is 25 parts of (d) to 75 parts of (a). This specific material is the only one of many similar materials that was effective in this invention. $[\text{CH}_2 = \text{CH}(\text{CH}_3)_2\text{Si}_2\text{O}$ was too volatile while

35 $[(\text{C}_6\text{H}_5)_2(\text{CH}_2 = \text{CH})\text{Si}]_2\text{O}$ and $[\text{CH}_2 = \text{CH}(\text{CH}_3)_2\text{SiO}]_2\text{SiCH}_3(\text{C}_6\text{H}_5)_2,$

although non-volatile, reduced the mechanical properties of the cured resin. This material is easily prepared by the same methods as indicated for the component (b) above.

40 Generally, for a two-component system, the component (d) is mixed into one package with a small portion of the base resin (a) and the catalyst required for cure. The remainder of the base resin (a) and the crosslinker (b) are mixed together to form a second package. The means for and manner of mixing these individual materials are not critical provided the mixtures are rendered homogenous. The two packages can then be mixed together at the appropriate time 45 for their use and cast into place. Upon heating, the composition cures. If other materials are to be mixed with the composition, they should be incorporated in to the individual packages during their preparation rather than adding those materials at the final mixing of the whole composition. Other materials that can be incorporated in the resin composition of this invention are conventional fillers such as glass fibers, finely divided silica, crushed quartz, powdered glass, asbestos talc, carbon black, iron oxide, titanium oxide, magnesium oxide or mixtures thereof. 50 Also included are pigments, dyes, oxidation inhibitors, cure inhibitors and release agents.

The curable composition can be employed in any conventional manner for casting or impregnating.

The components (a), (b), (c) and (d) are mixed together with any of the above desired 55 additives and mixed to homogeneity. The mixture is then fabricated into the desired form and cured, usually at elevated temperatures, for example, 100-150°C. It may be desirable in some cases to post-cure the cured material at elevated temperatures, for example, up to 200°C.

The accompanying drawing shows the effect of varying amounts of $(\phi\text{ViMeSi})_2\text{O}$ fluid in the 60 resin. The drawing is a graph illustrating variation in flux strengths (PSI) as a function of % base resin/remainder $(\phi\text{ViMeSi})_2\text{O}$ in part two.

The following examples are by way of comparison with the systems currently in the prior art. The examples are not intended as limiting the invention delineated in the claims.

Example 1

65 A base resin was prepared consisting of 75 mol percent of monophenylsiloxy units and 25

65

mol percent of vinyldimethylsiloxy units and was designated "A". Various types of crosslinkers designated "B", "C" and "D" respectively were prepared and mixed with A according to conventional techniques in the amounts shown in Table I below. The mixture of B with A is the example of the prior art shown in Mink *et al.*, U.S. Patent No. 3,944,519 at Table II, middle 5 column. Component B is $[\text{H}(\text{CH}_3)_2\text{SiO}]_2\text{Si}(\text{C}_6\text{H}_5)_2$; Component C is



and component D is 35 mole percent of diphenylsiloxy units 55 mole % of HCH_3SiO units and 10 10 mole percent of $(\text{CH}_3)_2\text{SiO}_{1/2}$ units. The catalyst was 1% $[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{PtCl}_2$ in toluene. Runs 1, 10 2 and 3 are outside the scope of the invention and represent the prior art.

Runs 4, 5 and 6 illustrate the invention and show the effect of the addition of component (d): $(\text{CH}_2 = \text{CH}(\text{CH}_3)_2\text{SiO})_2\text{Si}(\text{C}_6\text{H}_5)_2$. Two-part compositions were prepared wherein part one was the base resin (a) and the crosslinker (b) and the second part was the component (d) and the catalyst 15 15 and a small amount of component (a) as a carrier. The ratio of part one to part two was 10:1. The results are shown in Table II below.

Example 2

This example serves to illustrate the comparison between the prior art diluent $(\phi\text{ViMeSi})_2\text{O}$ and 20 the present diluent. As the amount of the prior art diluent is increased, the flex strength of the resulting resin is reduced. The increase in diluent is to decrease the viscosity so that the base resin can be easily handled.

Runs 7, 8 and 9 in Table 3 below show the use of $(\phi\text{ViMeSi})_2\text{O}$ as the reactive diluent, 25 wherein ϕ is C_6H_5- , Vi is $\text{CH}_2 = \text{CH}-$ and Me is CH_3- . Two-part compositions were again prepared wherein one was the base resin (a) and the second part was $(\phi\text{ViMeSi})_2\text{O}$, the catalyst and a small amount of component (a) as a carrier. The ratio of part one to part two was 10:1. The catalyst was the same as used in Example 1.

TABLE I

	Run No.	Parts A	Parts B	Parts C	Parts D	ppm cat
35	1	74.3	25.7			10
	2	81.4		18.6		10
	3	70			30	10

TABLE I CONTINUED

	Run No.	Visc P's At 25°C uncured	Cured flex Strength psi	Cured tan modulus psi $\times 10^6$	Cured sec modulus psi $\times 10^6$	Ratio tan/sec
45	1	3.0	5500	1.25	0.163	7.67
	2	3.0	7500	1.40	0.50	2.80
	3	>40.0	7500	1.54	0.85	1.81

TABLE II

	Run No.	Total Parts A	Total Parts B	Total Parts C	Total Parts D	parts Component (d)	Cat ppm
55	4	78.3	29.2			2.5	10
	5	86.2		21.3		2.5	10
	6	74			33.5	2.5	10

TABLE II CONTINUED

Viscosity Pa's at 25°C of part one.	Cured flex Strength psi	Cured tan Modulus $\times 10^6$	Cured sec modulus $\times 10^6$	Ratio tan/ sec	
5.0	3255	0.933	0.128	7.29	5
10.0	6133	1.27	0.428	2.97	10
5.0	7543	1.72	1.01	1.69	

TABLE III

Total Parts No. A	Total Parts B	Total Parts O_2	Cat ppm	Pa's Viscosity of part one at 25C.	
7	79.2	28.2	1.67	10	3.3
8	76.6	30.2	3.33	10	2.1
9	74.0	31.0	5.00	10	water thin

TABLE III CONTINUED

Pa's Viscosity of all Components at 25C Run No.	Cured Flex Strength psi	Cured tan Modulus $\times 10^6$	Cured sec Modulus $\times 10^6$	Ratio tan/ sec	
7	17.8°	3434	.796	.128	6.2
8	.48	1667	.259	.129	2.00
9	water thin	549	.042	—	—

* Unacceptable For Handling.

40 CLAIMS

- An improved curable composition consisting essentially of a mixture of (a) an organopolysiloxane containing from 67 to 85 mol percent $\text{C}_6\text{H}_5\text{SiO}_{3/2}$ units and 33 to 15 mol per cent of $\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{SiO}_{1/2}$ units, said organopolysiloxane having an average of at least 8 silicon atoms per molecule;
 - a silicon hydride-containing polysiloxane crosslinker for (a), the component (b) being present in an amount sufficient to provide about 0.9 to 1.1 mol of silicon hydride per mol of $\text{CH}_2 = \text{CHSi}-$ present in (a) and (d);
 - a platinum catalyst in an amount sufficient to catalyse the reaction of the silicon hydride with the $\text{CH}_2 = \text{CHSi}-$; and
 - a reactive diluent having the formula $[\text{CH}_2 = \text{CH}(\text{CH}_2)_2\text{SiO}]_2\text{Si}(\text{C}_6\text{H}_5)_2$.
2. A curable composition as claimed in claim 1, wherein the platinum catalyst (c) is present in an amount sufficient to provide at least 0.1 part by weight platinum per million parts of the combined weight of (a), (b) and (d).
3. A curable composition as claimed in claim 1 or 2 wherein the component (b) is present in an amount sufficient to provide substantially 1.0 mol of silicon hydride per mol of $\text{CH}_2 = \text{CHSi}-$ in (a) and (d).
4. A curable composition as claimed in any of claims 1 to 3 wherein the component (d) is present in an amount of from 20 to 50 parts by weight corresponding of from 80 to 50 parts by weight of the component (a).
5. A curable composition as claimed in claim 4 wherein the amount of (d) present is 25 parts by weight and there are present 75 parts by weight of (a).
6. A curable composition as claimed in claim 1 substantially as here described with reference to any of the specific examples.